Sulfonated poly(ether sulfone) based sulfonated molybdenum sulfide composite membranes: Proton transport properties and direct methanol fuel cell performance

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Proton Conductivity

A four-probe AC impedence spectroscopy has been employed to measure in-plane proton conductivity for a series of composite membranes under 100% relative humidity. Test sample with required size was clamped in BekkTech LLC conductivity cell having inbuilt four platinum probes. Conductivity cell was placed in ESPEC humidity and temperature chamber (SH-242) and connected with a single channel potentiostat (BioLogic, SP-150). Each membranes sample was scanned over a frequency range of 1Hz to 1MHz from 30 to 80°C. The membrane area resistance was obtained by Nyquist plot, through the intersection of high-frequency intercept with real axis and proton conductivity was calculated using the following formula:

$$\text{Proton conductivity } (\sigma) = \frac{d}{R \times T \times W} \text{ (S/cm)} \cdots\cdots (1)$$

Where R is the test sample resistance obtained from the real axis of the impedance spectra, d is the distance between probes in conductivity cell (0.425cm), T and, W are the thickness and width of test sample, respectively.

The activation energy for proton conduction was measured by using linear Arrhenius relation between ln of proton conductivity and temperature (1000/T). following equation is used to calculate activation energy for proton conduction:

$$E_a = b \times R \cdots\cdots (2)$$

Where E_a is the activation energy (kJ mol^{-1}) for proton conduction, b is the slope of linear regression of Arrhenius plot (ln σ vs. 1000/T) and R is the gas constant (8.314 JK^{-1} mol^{-1}).

Linear swelling ratio

The linear swelling ratio (LSR) of membrane samples was calculated taking the dimensional difference of wet and dry membrane samples using the below equation:

$$\text{LSR} = \frac{D_{wet} - D_{dry}}{D_{dry}} \times 100\% \quad \text{.....} \quad (3)$$

Where D_{vet} and D_{dry} are the dimensions of wet and dry membranes, respectively.

Data for water uptake, IEC, and linear swelling ratio were recorded with three different membrane samples and average value for WU, IEC, and LSR is presented in this study.

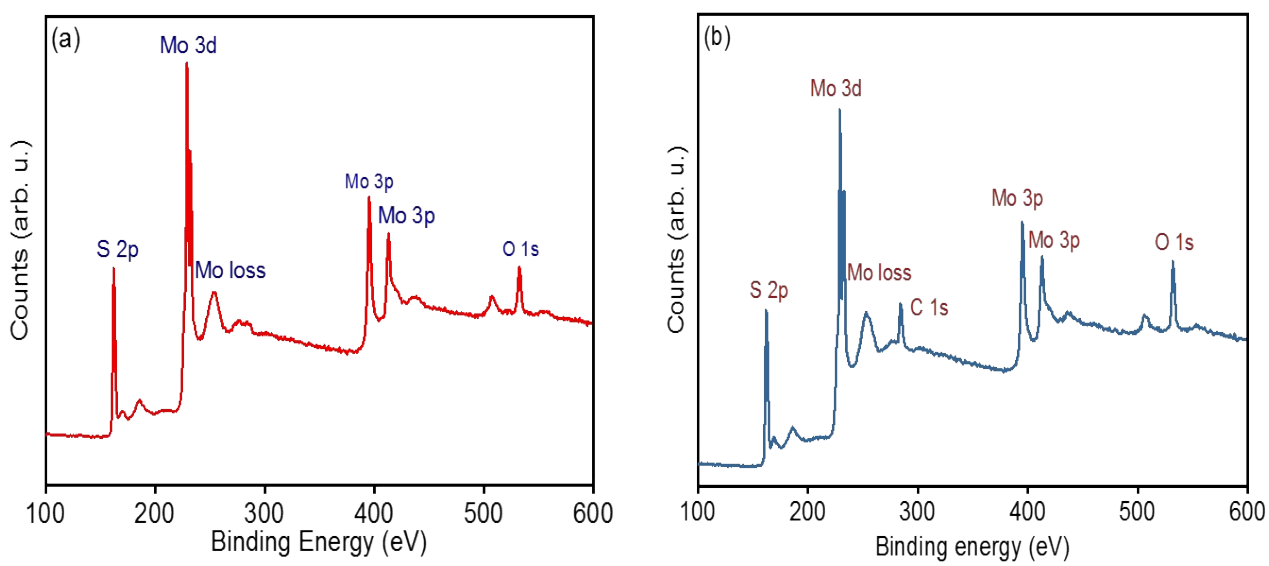

Fig. S1 XPS spectra of MoS_2 (a) and s-MoS_2 (b).

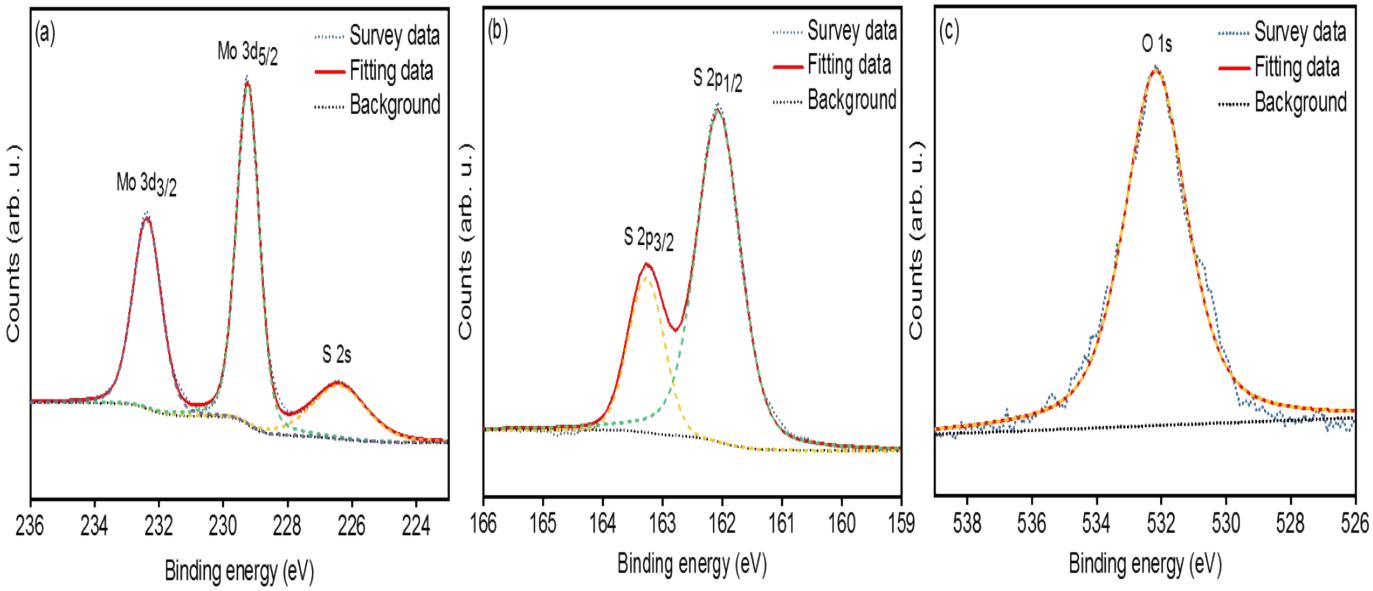

Fig. S2 XPS spectra of MoS_2: Mo 3d peak (a), S 2p peak (b), and O 1s peak (c) at high resolution.

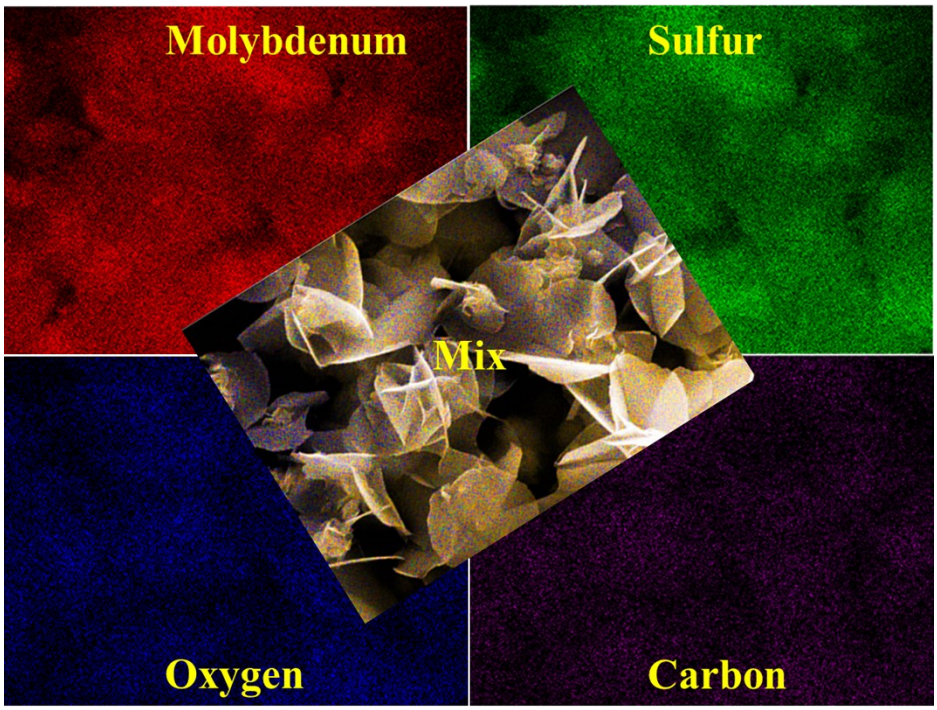

Fig. S3 Elemental mapping for s-MoS_2 to verify sulfonation reaction.

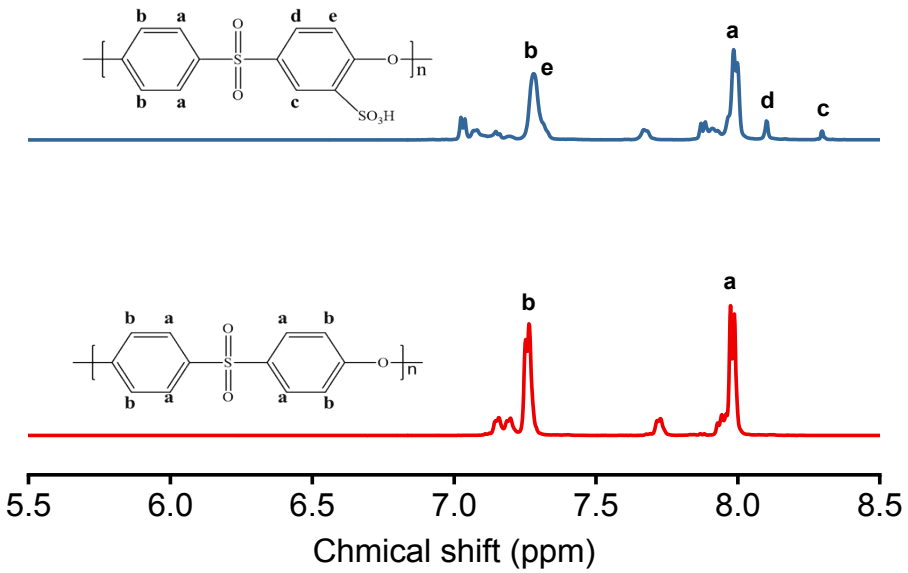

Fig. S4 ^{1}H-NMR spectra of poly(ether sulfone) and sulfonated poly(ether sulfone).

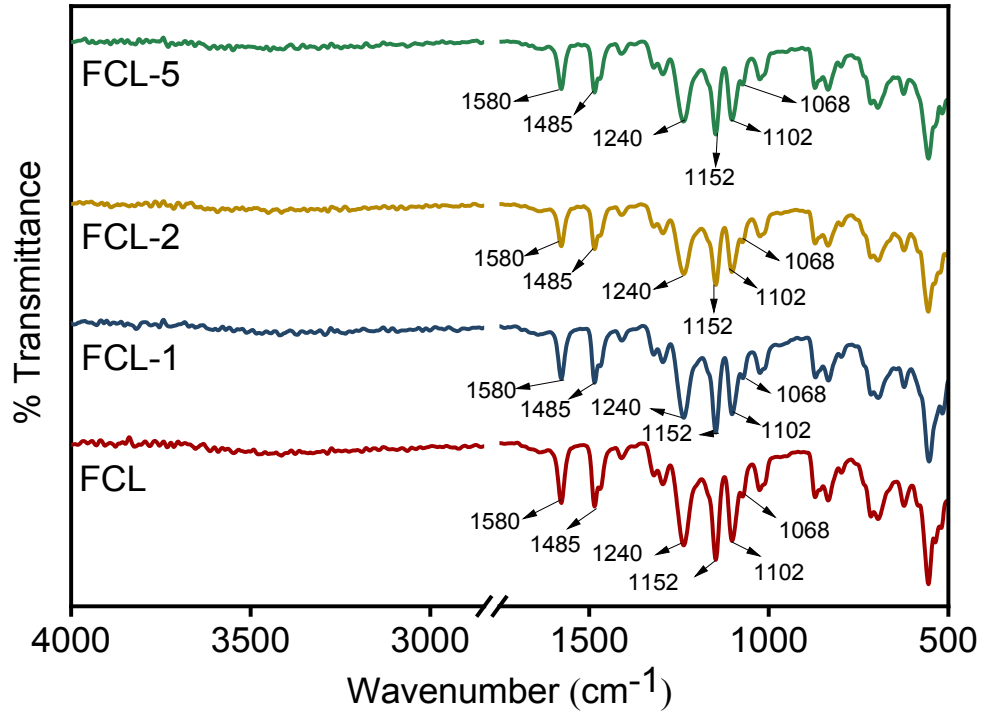

Fig. S5 FTIR-ATR spectra for pristine sPES and composite membranes for functional group analysis.

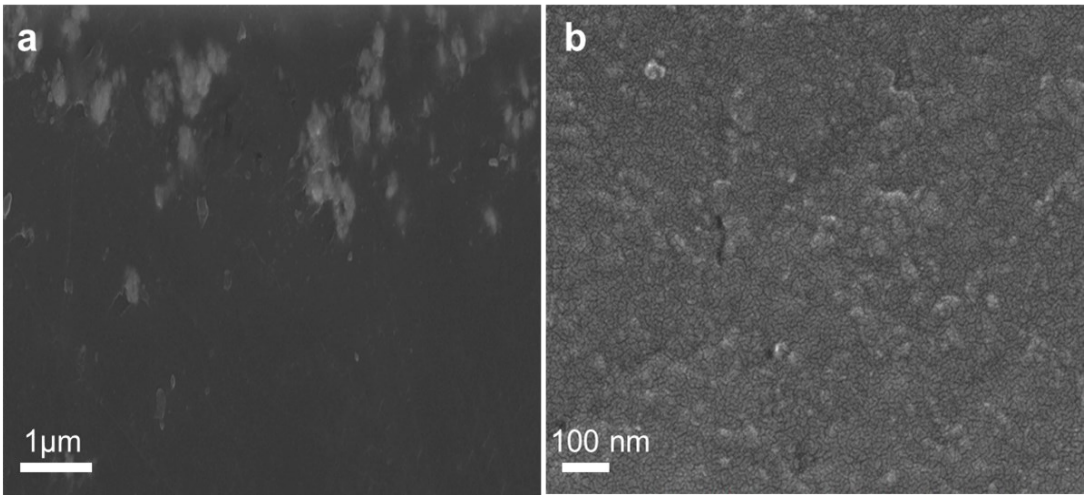

Fig. S6 Surface SEM images for 6 wt. % composite membrane at different magnifications.

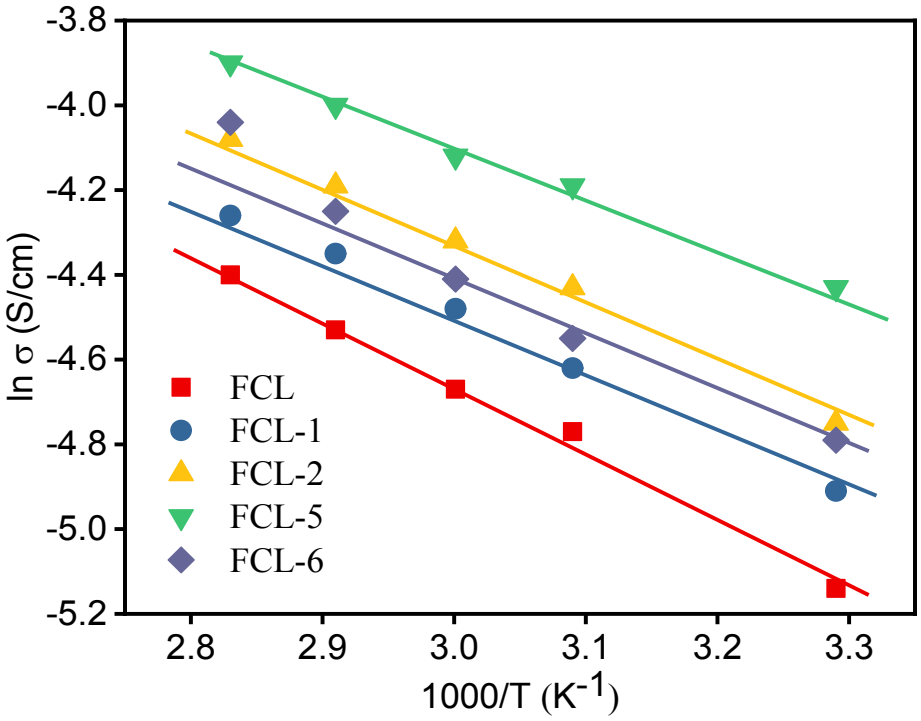

Fig. S7 Arrhenius plot of thermal dependence for FCL membranes.

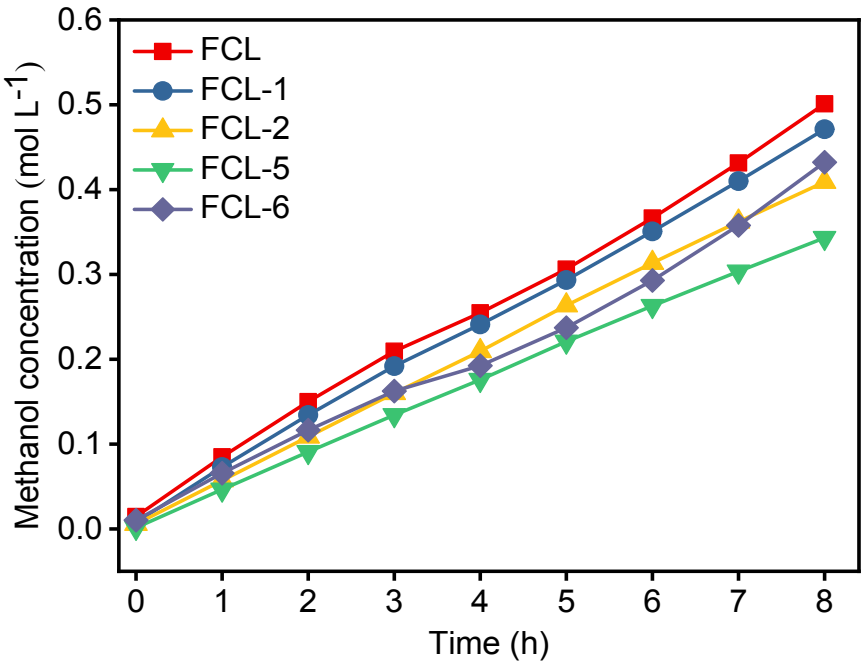

Fig. S8 Methanol concentration profile in diffusate compartment for different membranes (Experiment carried out at 30°C with 2 mol/L initial concentration of methanol in feed compartment).

Table S1 Mechanical analysis of synthesized membranes in terms of their tensile strength and elongation at break (Fully hydrated samples were used).

Membrane	Elongation at Break (%)	Tensile strength (MPa)	Elastic modulus (MPa)
FCL	51.40	15.21	1.02
FCL-1	53.91	16.94	1.52
FCL-2	55.09	20.22	1.75
FCL-5	65.85	24.53	1.97
FCL-6	57.37	22.11	1.14